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(54) Title: **ELECTROACTIVE POLYARYLAMINE-TYPE COMPOSITIONS**

(57) Abstract: Tri-aryl amines having ion-chelating side chains such as polyethoxy glycol groups, are useful charge transport materials, and may be oligomerised or polymerised to form conducting films or tracks. Uses in solid polymer electrolytes in opto-electronic or electrochemical devices are foreseen.

ELECTROACTIVE POLYARYLAMINE-TYPE COMPOSITIONS

This invention concerns organic materials, especially electroactive organic materials, such as polyarylamine-type molecules and methods for their preparation and
5 films thereof. Such molecules when incorporated into films and/or composite layers are useful as charge transport materials (CTMs) in optoelectronic and electrochemical devices, including electroluminescent displays, batteries and solar cells.

There is a continuing need for the development of organic solid-state electrolyte
10 and transport materials as replacements for traditional liquid electrolytes. Liquid electrolytes often introduce difficulties in the scale-up and sealing of active devices during manufacture, and solid electrolytes are therefore preferred. For example in display technology, where the recombination of injected electrons and holes produces light emissions, a variety of CTMs have been developed based on particular classes of organic
15 molecules such as poly(p-phenylene vinylene) PPV (C R Towns et al , WO 00/53656), polyfluorenes, perylenes and triarylamine.

A particular example of a solar cell application is the dye-sensitised cell developed by Grätzel *et al.* (*Nature*, 1991, 353, 737), where a high-surface area, dye-
20 coated semiconducting working electrode is in contact with a charge-carrying, mobile redox couple. The action of the redox couple, usually I_3^-/I_2 , is used to complete the charge transfer process by injecting an electron into the photo-oxidised dye to restore it to the ground-state. In early work, cells were made with the redox couple dissolved in a liquid electrolyte. More recently, increasing efforts have been made to find solid-
25 electrolyte alternatives, for example by incorporating gelling agents or organic polymer CTMs (Grätzel *et al.* *Nature*, 1998, 395, 583).

However, solid electrolytes, especially those developed for hole or electron-transport, often suffer from poor conductivity compared to their liquid-phase
30 counterparts. Other potential problems include excessive sensitivity to e.g. water and oxygen, mismatch of relevant energy levels with other cell components, and poor processibility. There is also a need for materials to remain amorphous over as wide a temperature range as possible as this assists in conductivity and optical transparency.

Thus to improve efficiencies of energy conversion in optoelectronic devices and electrochemical cells, and improve manufacturability, a variety of CTMs are required.

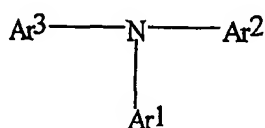
Poly-alkylfluorenes or their copolymers with other aryl moieties have been intensively studied owing to their efficient photoluminescent properties and stability as blue light emitting components in organic LEDs. In addition, there are literature reports of fluorene-based polymers exhibit interesting transport properties. Fluorene-triarylamine copolymers demonstrate high charge carrier mobilities that approach hole mobilities of the standard glassy films of aryl diamines (E.P. Woo, *et al.*, WO 9733193).

To improve the amorphous character (and hence conductivity, transparency etc) of these types of materials, spiro versions of triarylamine have been developed e.g. spirobifluorene triarylamine derivatives (U. Bach *et al.*, *Adv. Mater.*, 2000, 12, 1060; Kruger, *et al.*, *Adv. Mater.*, 2000, 12, 447). Furthermore, copolymeric triarylamine and polythiophene derivatives have proven advantageous in raising the device efficiency of solid state organic photovoltaic devices fabricated using polymer composites which facilitate charge separation (J.J.M. Halls *et al.*, *Adv. Mater.*, 2000, 12, 498; J.J. Dittmer *et al.*, *Adv. Mater.*, 2000, 12, 1270). Copolymeric triarylamine derivatives have found applications as hole transporting materials in organic electroluminescent devices (E.P. Woo, *et al.*, WO 9733193).

Grätzel *et al* developed a spirocyclic triarylamine (OMeTAD) as a hole-transport material for use in a dye-sensitised photovoltaic cell (*Nature*, 1998, 395, 583). Poly(triarylamine)s have been used by Thelakkat *et al.* (*Synth. Met.*, 1999, 102, 1125) in photovoltaic cells consisting of an inorganic nano-crystalline TiO₂ layer with suitable dyes for light absorption. Triarylamine have also been employed as small molecule hole transport materials in such cells (Hagen, *et al.*, *Synth. Met.*, 1997, 89, 215). Advantageously, ion-supporting polymer electrolytes have been shown to enhance performance of organic optoelectronic devices that rely on redox couples. Light emitting, polymeric electrochemical cells (LECs) are one such example (Pei, *Science*, 1995, 269, 1086). Ion-supporting side chains attached to light emitting polymers have enhanced device efficiencies in LECs (Pei, *J Am Chem Soc.*, 1996, 118, 7416).

We disclose in this invention a new class of small molecule triarylamine derivatives with variable redox potentials, high tendency to form amorphous organic films, good thermal and chemical stability, good processibility, and related favourable properties. These monomeric materials are conveniently incorporated in conjugated
 5 homo- and copolymers which also possess the above favourable properties and good processibility as organic thin films.

In accordance with a first aspect of the present invention, a material for charge transporting comprises tertiary amine molecules or oligomers or polymers thereof,
 10 wherein said molecules comprise at least one moiety represented by the general formula (1):



(1)

wherein Ar^1 , Ar^2 and Ar^3 are independently substituted or unsubstituted aromatic or hetero-aromatic rings or fused or otherwise conjugated derivatives thereof; wherein one
 20 or more of Ar^1 , Ar^2 and Ar^3 is derivatised with one or more ion-chelating groups selected from $[-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OCH}_3]$, $[-\text{O}(\text{CH}_2\text{CH}_2)_n\text{OCH}_3]$, $[-(\text{CH}_2\text{CH}(\text{R})\text{O})_n\text{CH}_2\text{CH}_2\text{OCH}_3]$ and $[-\text{O}(\text{CH}(\text{R})\text{CH}_2)_n\text{OCH}_3]$; wherein n is an integer from 0 to 10, preferably 2 to 10, more preferably 2 to 4; wherein R is straight or branched alkyl chain of 1 to 10 carbon atoms, preferably of 1 or 2 carbon atoms; and wherein the
 25 ion chelating groups comprise side chains in oligomeric or polymeric structures.

The ion chelating side chains are based on the repeat unit $[-\text{OCH}_2\text{CH}_2-]$. Side chain branching and/ or the inclusion of $[-\text{OCH}_2\text{O}-]$ repeat-units, are advantageous to inhibit crystallisation after metal ion complexation. The side chains contain preferably 3
 30 or more $[-\text{OCH}_2\text{CH}_2-]$ and most preferably 3 units terminating in OR (R = alkyl of up to 10 carbon atoms, e.g. methyl) containing 4 oxygen atoms for cation chelation. Crown ethers may also be designed accordingly. Other side chain designs may be made according to the specific need for cation binding. Alternative design features could be incorporated into monomers and polymers to favour anion binding.

We have also found that a disadvantage of some small molecule materials carrying short poly-ethoxy glycol (PEG) side chains is that the material is likely to crystallise in the presence of e.g. Li ions. This may be overcome by increasing the disorder in the side chains or by having a range of molecular weight of polymeric material carrying the ion supporting side chains or by using a crown ether. The usefulness of disorder in polymer electrolytes has previously been proposed by Colley, *et al.*, (*J Mater. Chem.*, 1999, 9, 1661). Nonetheless, no operable CTMs of the type realised by the present inventors have previously been disclosed.

10

The materials of the present invention exhibit high conductivities due to the presence of an extended conjugated structure. Preferably, the material exhibits extended π or mixed π -lone pair conjugation. This may be for example, by way of Ar-N-Ar type linkages, where the Ar groupings may themselves comprise extended conjugation through the connection of aromatic ring moieties with unsaturated groups.

15

By arranging for the ion-chelating groups to form side chains in oligomeric and polymeric species the conductivity of the material is not compromised. This is in contrast to some prior tri-aryl amine species where alkoxy type groupings are used to connect adjacent amine groups, e.g. EP 0550161 A1. In such molecules, the alkoxy groups are of the form $-\text{OCH}_2-$ so π -lone pair conjugation is interrupted and there is no continuous conduction pathway.

20

Preferably, at least one of Ar^1 , Ar^2 or Ar^3 is substituted by alkyl, alkoxy, ether, halo alkyl, amino alkyl, aryl or heteroaryl, where any alkyl group is straight or branched chain of 1-10 carbon atoms. In a particularly preferred embodiment, at least one of Ar^1 , Ar^2 or Ar^3 is twice substituted with a straight or branched alkyl chain of 1-10 carbon atoms, for example octyl.

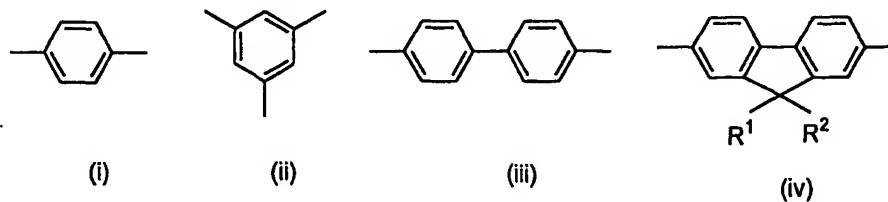
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Preferably, at least one of Ar^1 , Ar^2 or Ar^3 is substituted in the ortho- or para-position by an alkoxy group, most preferably in the para- position. Suitably, the alkoxy group is a short chain alkoxy group, for example from 1 – 4 carbon atoms, and most preferably methoxy. Although not wishing to be bound by any theory, it is thought that

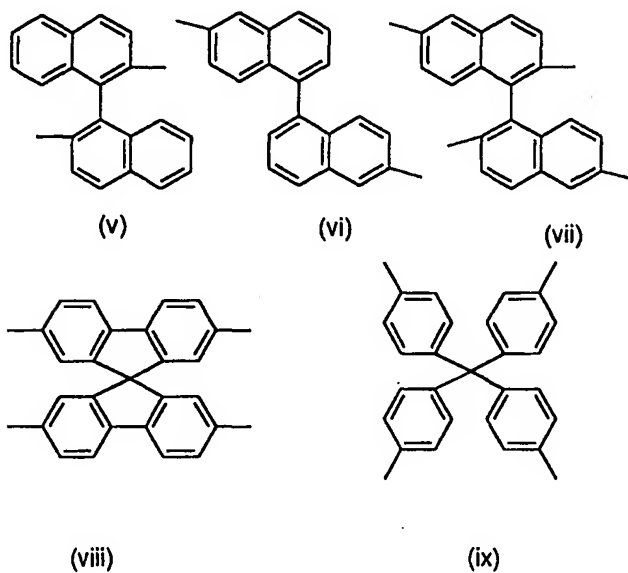
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the presence of a short chain alkoxy group in the para- position increases the ease of oxidation of the material, thus facilitating hole conduction.

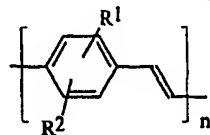
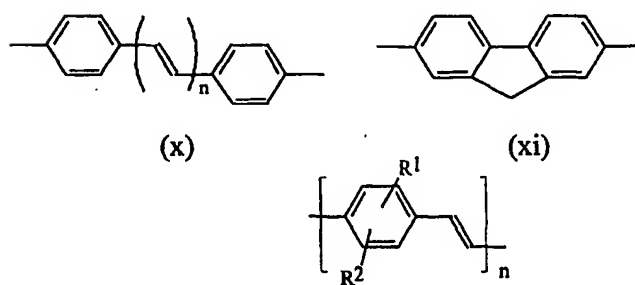
Preferably, at least one of Ar^1 , Ar^2 or Ar^3 is selected from structures (i) to (xii)



5



10



(xii)

15

wherein R^1 and R^2 are independently selected from, hydrogen, halogen, alkyl, alkoxy, ether, amino alkyl, aryl or heteroaryl, in which any alkyl group is straight or branched

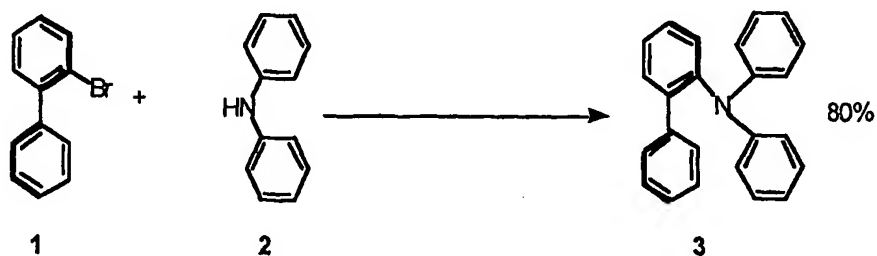
chain of 1 to 10 carbon atoms; wherein n is an integer; and wherein any of (i) to (xii) may be substituted or unsubstituted.

Although not as effective, a group with the structure of an ion-chelating group
5 may be used as a linking group between moieties of general formula 1. If such a group is used it should be in the ortho- or para- position and not in the meta- position. Most preferably if such a linking group is used, it is in the para- position.

The molecules and polymers of this invention may be prepared by essentially
10 analogous techniques to those known in the literature. Preparative routes are described in detail below and these can be adapted by the skilled person as necessary to yield particular products. The molecules and polymers are not restricted to any single preparative method.

GENERAL PREPARATIVE METHODS

Triaryl amines can advantageously be prepared by Pd-mediated amination reactions (H. Yang and S. L. Buchwald, *J. Org. Chem.* 1999, 579, 125). 2-bromobiphenyl and 2-amino biphenyl were chosen to demonstrate coupling procedures. Employing $P(t-Bu)_3$ as a ligand in the reactions of primary aryl amines with excess aryl halides, or secondary amines with aryl halides, is known to produce the corresponding triaryl amines in high yields (87-96%) (J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaugnessy and L. M. Alcazar-Roman, *J. Org. Chem.*, 1999, 64, 5575). The aminations of the 2-bromobiphenyl (1) with one equivalent of the diphenylamine (2) using 1 mol% $Pd(OAc)_2$ and 1 mol% $P(t-Bu)_3$ in NaO-t-Bu in toluene at 90°C gave the triarylamine (3) in a reasonable yield (80%) (Scheme 1)

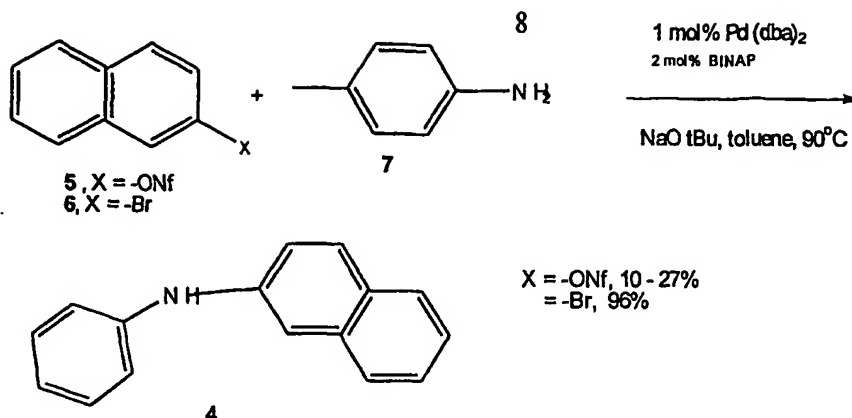


15

Scheme 1

As shown in the Scheme 2, the reactivity of the naphthyl nonaflate (4) is lower than that of the bromonaphthyl (5) in the same catalytic condition, giving the diarylamine (4) in 10-27% and 96% of yields, respectively.

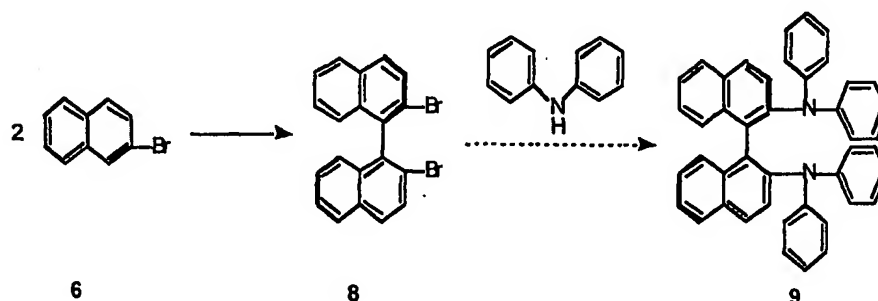
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Scheme 2

5 As shown in the Scheme 3, the binaphthyl-based triarylamine (9) could be synthesized along similar lines. Oxidative dehydrodimerisation of the aryl halides (6) in the presence of lead(IV) acetate in acetonitrile containing boron trifluoride is known to produce the binaphthylhalide (8) with unknown oligomers in an average yield (55%) (Scheme 3) but (9) was not successfully synthesized by this scheme.

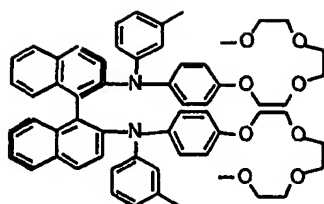
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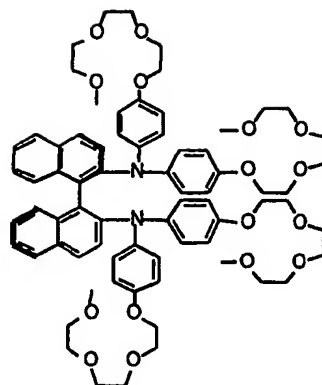
Scheme 3

15 Work on amination reactions has led us to synthesise the target molecules (10) and (11). The binaphthylhalide (8) from oxidative dehydrodimerisation of the aryl halides (6) in the presence of lead(IV) acetate in acetonitrile containing boron trifluoride has been obtained, followed by C-N bond formation in the halide (9). This leads to the molecules (10) and (11) with ion supporting side chains.

9

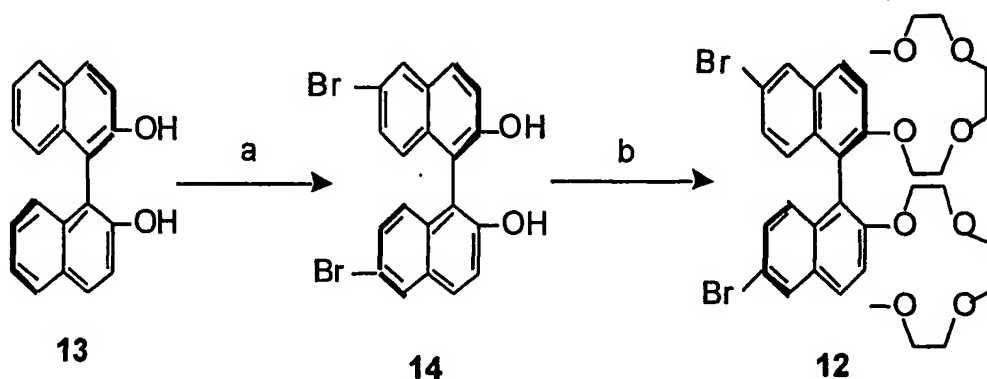


10



11

- Difficulties with the synthesis of the target molecule (9) led to the design of an alternative molecule (12) with trisethoxymethoxy substituents as ion supporting groups in both 2 positions. Bromination at both 6 positions in the diol (13) followed by conversion of the alcohol to the triethylene glycol methyl ether *via* substitution reaction of the alcohol (14) and the tosylated alcohol, gave the product (12) in 70% overall yield.

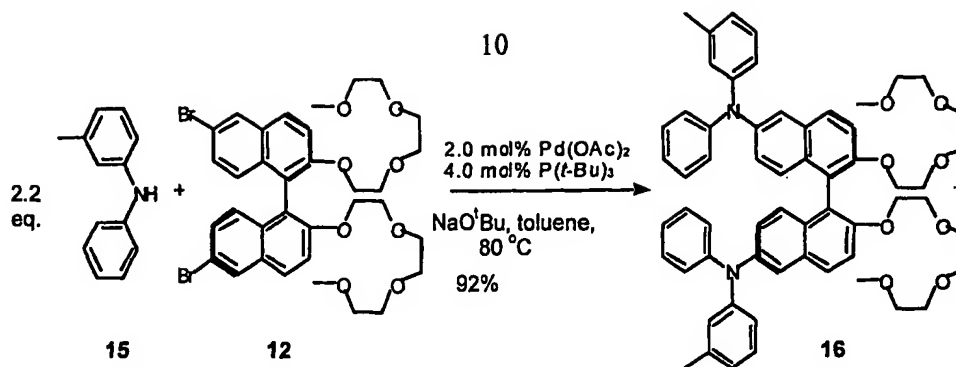


reagents; a) Br₂, DCM, r.t., 5h, 93%; b) i) KO^tBu, THF, 60 °C, 30 min; ii) TsO(CH₂CH₂O)₃CH₃, THF, 78 °C, 18 h, 75%

10

Scheme 4

- The alternative target molecule (16) was obtained by Pd-catalysed amination of (12) with diaryl amine (15) in a high yield (91%) in the presence of Pd(OAc)₂ as a catalyst and P(^tBu)₃ as a ligand (Scheme 5).

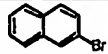
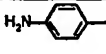
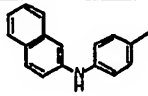
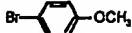

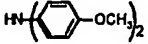
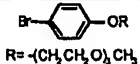
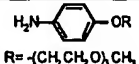
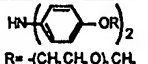


Scheme 5

5 Synthesis of spirocyclic triarylamine derivatives

Even though the $P(t\text{Bu})_3/\text{Pd}(\text{dba})_2$ catalyst is an attractive method for synthesis of diarylamines as well as triarylamines, the $\text{BINAP}/\text{Pd}(\text{dba})_2$ catalyst system is preferred for cross-coupling of variety of primary amines. This is because the use of $P(t\text{Bu})_3$ compared to BINAP requires much more demanding reaction conditions, such as sublimated halides and amines, air and moisture sensitivity of the ligand and the possibility of further aminations affording triarylamines. Thus, the $\text{BINAP}/\text{Pd}(\text{dba})_2$ catalyst system was applied to the coupling reactions of this invention. The diarylamines (17), (20) and (23) were synthesised by the Pd-catalysed amination of the corresponding halides (5), (18) and (21) with the amines (7), (19) and (22), respectively, in the presence of $\text{Pd}(\text{dba})_2$ and BINAP (table 1.1).

Table 1.1 BINAP/Pd-catalysed arylation of primary aryl amines

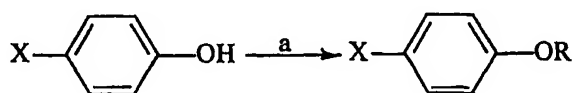
Entry	Halide	Amine	Product	mol % of Pd	Yield (%)
1	 (5)	 (7)	 (17)	1.0	96
2	 (18)	 (19)	 (20)	0.32	76
3	 (21)	 (22)	 (23)	2.0	87

- 5 Reaction conditions: 1.0 equiv. of ArBr, 1.2-1.3 equiv. of amine, 1.4 equiv. of NaO^tBu, catalyst Pd(dba)₂, ligand BINAP, 2.0 ratio of Pd to ligand, toluene, overnight, 90 °C.

- 10 2-Bromonaphthalene (6) instead of 2-naphthylnonaflate (5) was employed in the synthesis of (17), due to low reactivity of (5) as described above (Scheme 2), affording (17) in high yield (96%). Employing low amounts of catalysts gave (20) as a brown solid (76% yield). The brown solid was readily sublimed at 140 °C (0.2 mmHg) affording (20) as a white solid.

- 15 The substrates (30), (31) and (32) with a trisethoxymethoxy substituent as an ion supporting group were obtained by conversion of the alcohol to the tetraethylene glycol methyl ether *via* substitution reaction of the alcohol (24), (25) and (26) and the tosylated alcohol in 80-88% yields (Scheme 6).

20



24 X = Br

25 X = I

26 X = NH₂

27 X = Br

28 X = I

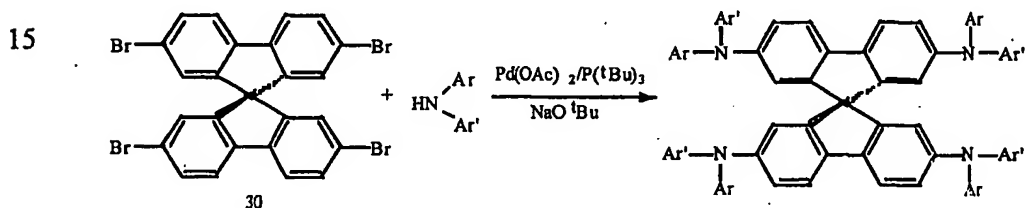
29 X = NH₂

Reagents; a) i) KO^tBu, THF, 60°C, 30 min; ii) TsO(CH₂CH₂O)₃CH₃, THF, reflux, overnight (27), 2h (28 and 29), 75%. Yields: (27) – 87%, (28) – 80%, (29) – 88%; R = – (CH₂CH₂O)₃CH₃.

Scheme 6

Synthesis of 2,2',7,7'-tetrakis-diarylamino-9,9'-spirobifluorenes





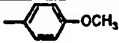
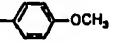


The efficacy of P(^tBu)₃ in amination of aryl halides with secondary amines to produce triarylamine has already been proven in many documents. Thus, as in the previous aminations (Scheme 5), the ligand was also applied to coupling reactions of the tetrabromo spirofluorene (30) and the diarylamines prepared above, affording four kinds of spirocyclic triarylamine derivatives (Scheme 7).



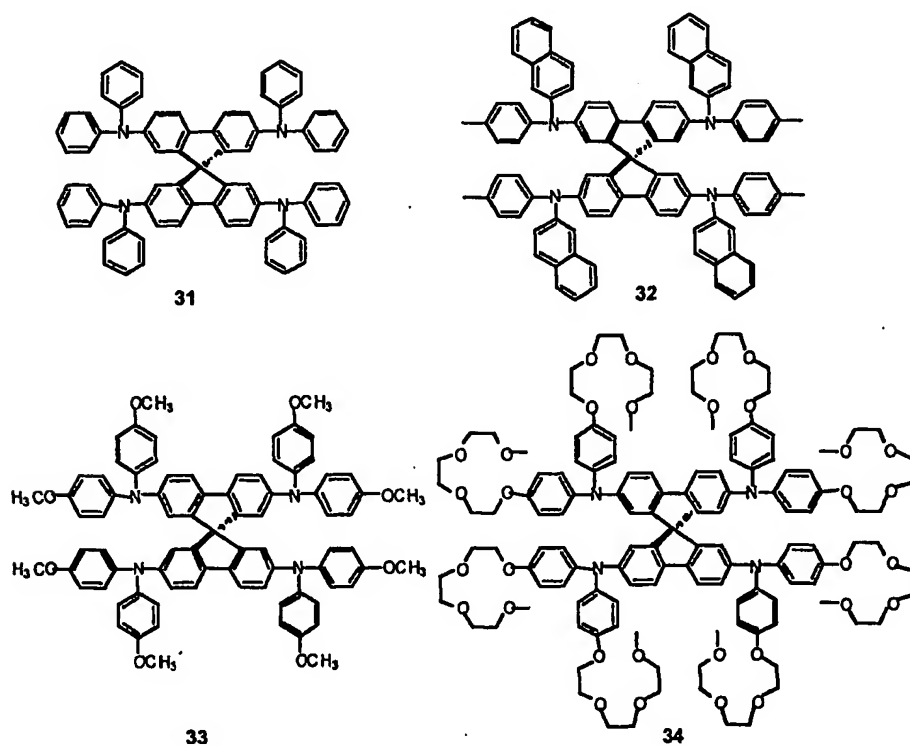
Scheme 7

Details of reaction variants are given in Table 1.2.

Table 1.2 Synthesis of spirocyclic triarylamine derivatives by $P(tBu)_3$ /Pd-catalysed arylation of secondary aryl amines

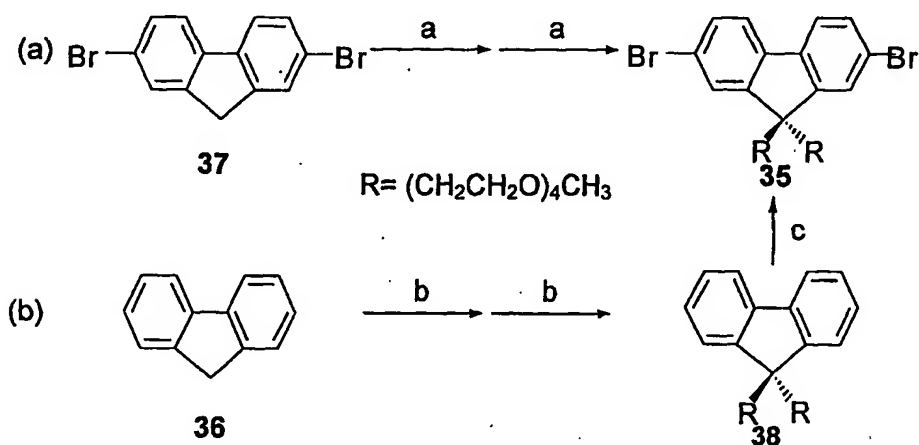
Number of product	eq. of Amine	Ar	Ar'	mol% of Pd	mol% of Ligand	Yield (%)
(31)	6.0			1.0	4.0	92
(32)	4.0			1.0	4.0	64
(33)	5.0			1.0	4.0	92
(34)	4.0	 R = $-CH_2CH_2O_3CH_3$	 R = $-CH_2CH_2O_3CH_3$	0.5	1.0	80

- 5 Reaction conditions: 1.0 equiv. of ArBr, 1.2 equiv. of NaO^tBu for amine, catalyst Pd(OAc)₂, ligand P(^tBu)₃, toluene, 3h (31 and 32), 2h (33), overnight (34), 90°C.



Synthesis of fluorene-based triarylamines

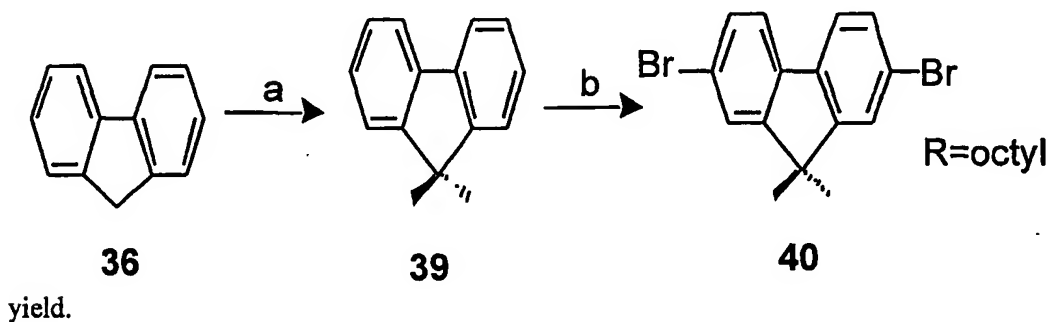
An attempt to synthesise (35) by the introduction of triethylene glycol methyl ether on the benzyl positions in dibromo fluorene (37) produced unknown side products as well as (35) in low yield (32%) [Scheme 8a]. Thus, the synthetic route for the
 5 synthesis of (35) was modified as shown above [Scheme 8b]. Conversion of the acidic protons to the triethylene glycol methyl ether *via* substitution reaction of the anionic carbon in fluorene (36) and the tosylated alcohol, followed by bromination in (38) gave (35) in 89% overall yield.



- 10 *Reagents*; a) i) KO^tBu, THF, reflux, 3h; ii) TsO(CH₂CH₂O)₃CH₃, THF, reflux, 3h, 32% (2 steps); b) i) *s*-BuLi, THF, -78 °C to r.t., 40 min.; ii) Ts(CH₂CH₂O)₃CH₃, THF, -78°C to r.t., 4h, 97% (2 steps); c) Br₂, DMF, 0°C, 10 min, 92%.

Scheme 8

Following the literature, the use of 2 equiv. of *n*-BuLi and octylbromide gave the dioctyl substituted fluorene (39), which was brominated affording (40) in 87% overall



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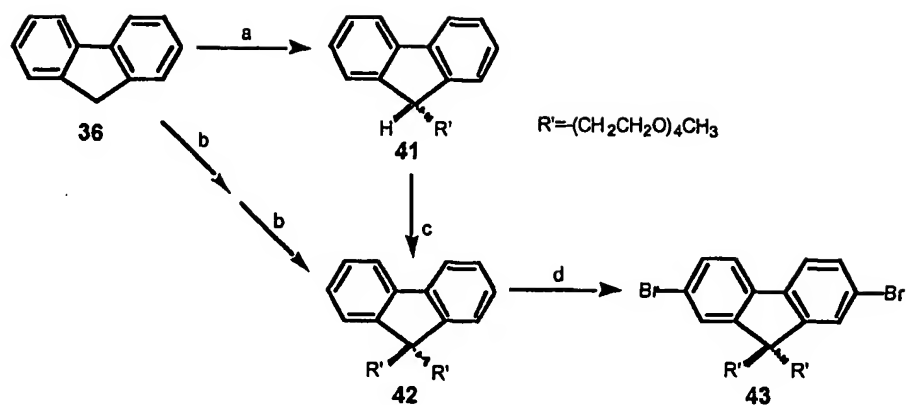
Reagents; a) i) 2 equiv *n*-BuLi, THF, -65°C, 1h; ii) 2 equiv octylbromide, THF, -65°C, 30 min., 94% b) I₂, THF, Br₂, overnight, r.t., 93%

Scheme 8c

10

As in the synthesis of the triethyleneglycol substituted fluorene (35), substitution reaction of the anionic carbon in the fluorene (36) and the tosylated tetraethylene glycol methyl ether (47) followed by bromination of the substituted fluorene (42) in the presence of bromine and iodine as a catalyst in DCM gave the product (43) in 52% overall yield (Scheme 9). Unlike the previous reactions using the tosylated triethylene glycol methyl ether (Scheme 7), bromination in DMF as a solvent without any catalysts as well as the substitution reaction showed low yields of 40% and 55 %, respectively. The use of 2 equiv *s*-BuLi and the tosylated alcohol (47) just produced the mono-substituted fluorene (41) in a low yield (35 %).

20



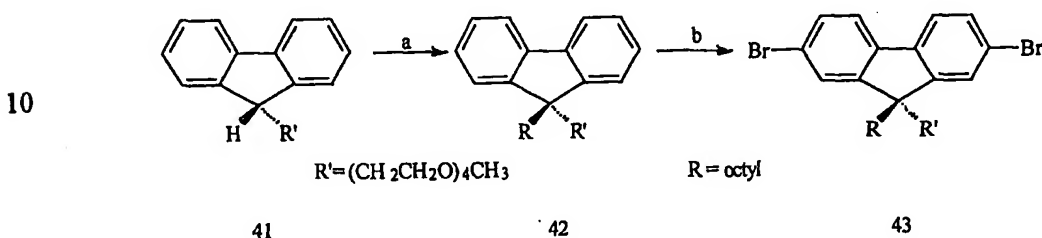
Scheme 9

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Reagents; a) i) 2 equiv *s*-BuLi, THF, -70 °C, 2h; ii) 2 equiv TsO(CH₂CH₂O)₄CH₃, THF, -70 °C, 4h, 35%; b) i) *s*-BuLi, THF, -70 °C, 1h; ii) TsO(CH₂CH₂O)₄CH₃, THF, -70 °C to r.t., 4h, ii) *s*-BuLi, THF, -70 °C, 1h, 55% (2 steps); c) i) *s*-BuLi, THF, -70 °C, 1h; ii) TsO(CH₂CH₂O)₄CH₃, THF, -60 °C to r.t., 4h, 89%; d) i) Br₂, DMF, 0 °C, 10 min, 40%; ii) I₂, DCM, Br₂, overnight, r.t., 94%.

10

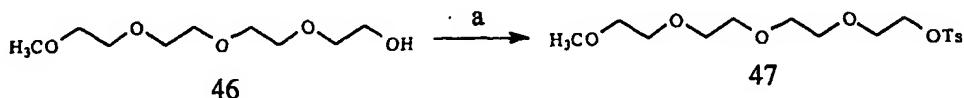
The substituted halide fluorene (43) was synthesised by further substitution reactions of the anionic carbon in the mono substituted fluorene (41) and octyl bromides followed by bromination of the fluorene (42) in 58% overall yield (Scheme 10). In order to increase the yield of bromination, the use of iodine as a catalyst was employed, but with no difference.



15 *Reagents*; a) i) *t*-BuLi, THF, -70°C, 2h; ii) octylbromide, THF, -68°C, 40 min., 89%; b) i) Br₂, DMF, 0 °C, 10 min, 65%; ii) I₂, DCM, Br₂, overnight, r.t., 64%.

Scheme 10

20 The tosylated alcohol (47) was produced from the commercially available triethylene glycol methyl ether (46) via a reaction with tosyl chloride under TEA employing catalytic amounts of DMAP yielding (47) in high yield (95 %) (Scheme 11).

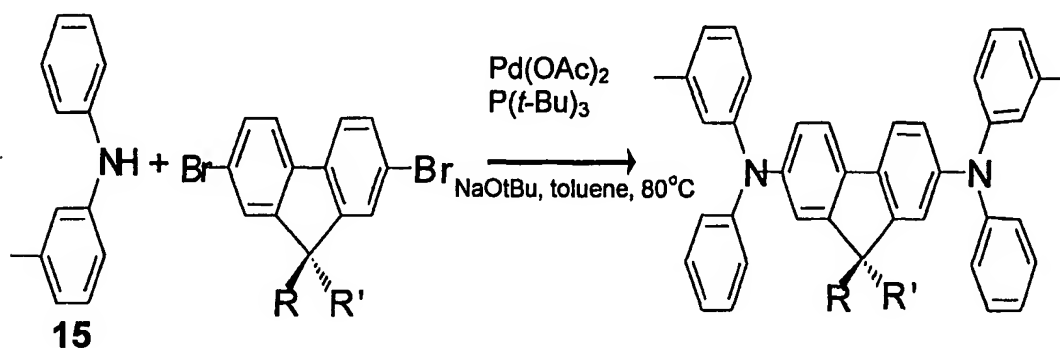


Reagents; a) tosyl chloride, TEA, cat. DMAP, overnight, 0°C to r.t., 95%

Scheme 11

Synthesis of 2,7-bis(3'-methyldiphenylamine)-9-bis(substituted) fluorene

As in the previous aminations (Scheme 7), the same catalytic systems was also used in the coupling reactions of the dibromofluorenes (35), (40), (42) and (44) prepared above and the diarylamines (15), affording four kinds of the triarylaminefluorene derivatives (48)-(51).



Scheme 12

Details of the synthetic results of Scheme 12 are shown in Table 1.3.

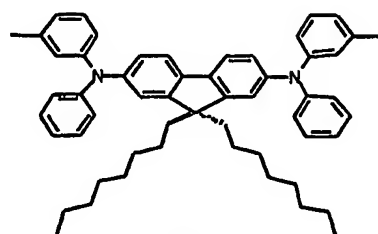
Table 1.3 Synthesis of triarylaminefluorene derivatives by P(*t*Bu)₃/Pd-catalysed arylation of secondary aryl amines

Number of product	eq. of Amine	R	R'	mol% of Pd	mol% of Ligand	Yield (%)
48	4.0	octyl	octyl	0.5	1.0	91
49	5.0	octyl	(CH ₂ CH ₂ O) ₃ CH ₃	0.5	1.0	95
50	4.0	(CH ₂ CH ₂ O) ₄ CH ₃	(CH ₂ CH ₂ O) ₄ CH ₃	0.5	1.0	96
51	4.0	(CH ₂ CH ₂ O) ₃ CH ₃	(CH ₂ CH ₂ O) ₃ CH ₃	1.0	2.0	93

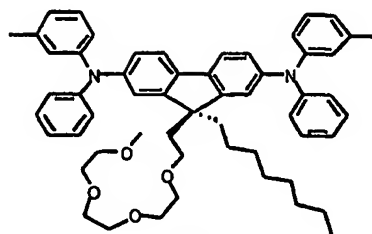
Reaction conditions: 1.0 equiv of ArBr, 1.2 equiv of NaO^{*t*}Bu for amine, catalyst Pd(OAc)₂, ligand P(*t*Bu)₃, toluene, 2h- 4h, 90 °C.

Unlike the case of synthesis of electron donating substituted spirocyclic triarylamine derivatives (33) and (34), aminations of fluorenes having ethylene glycol

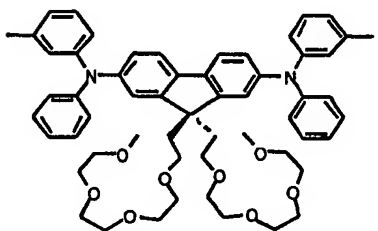
oligomer(s) did not produce any extra new spots on TLC, providing good separation by silica chromatography.



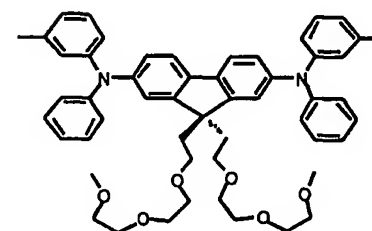
48



49



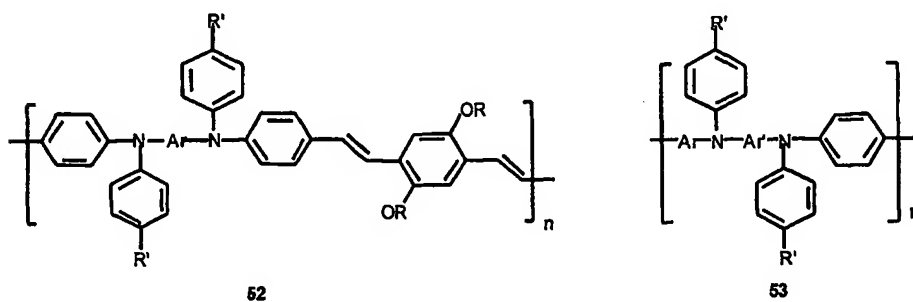
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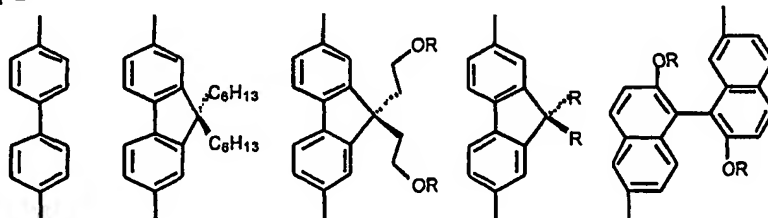
51

Polymer synthetic work

The synthesis of triaryl amine polymers (52) and (53) by Pd-catalysed aminations has also been carried out. The monomer units in (52) and (53) can be selected from the results of the study of small molecular CTMs prepared in this invention. In order to avoid phase separation in macromolecules, the CTMs are preferably covalently linked to the ion supporting polyelectrolyte component.

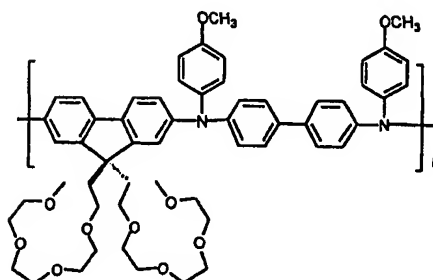
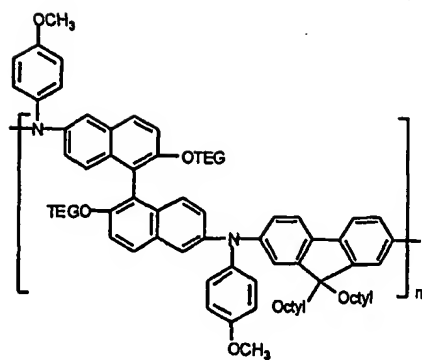
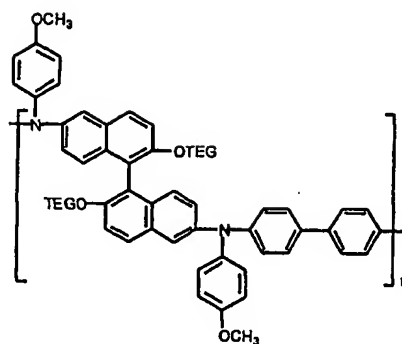
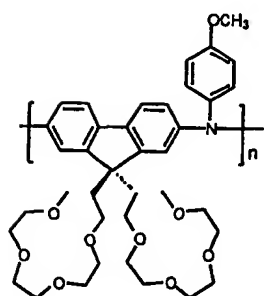
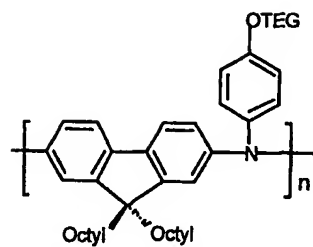
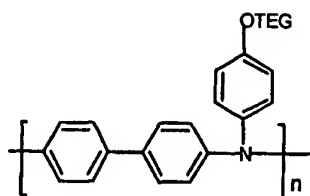


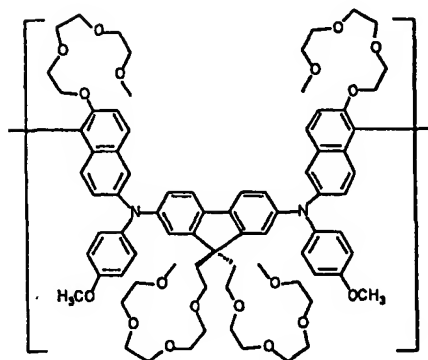
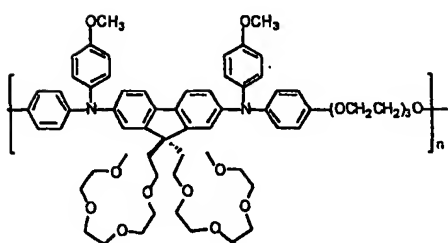
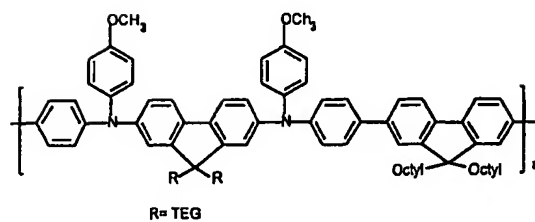
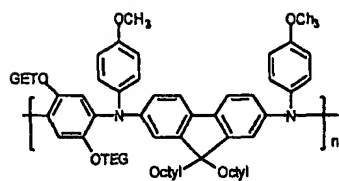
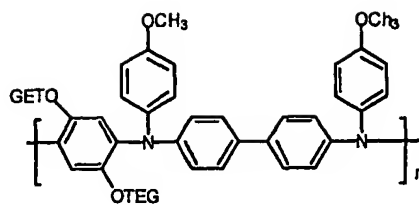
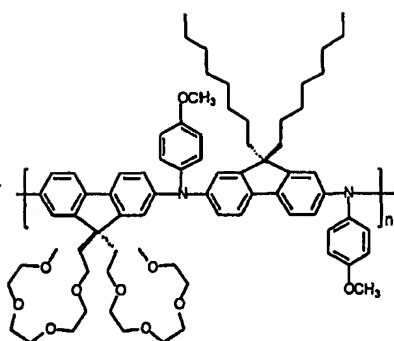
$R = (CH_2CH_2O)_mCH_3$, $m = 1-4$
 $R' = H$, alkyl
 Ar or $Ar' =$

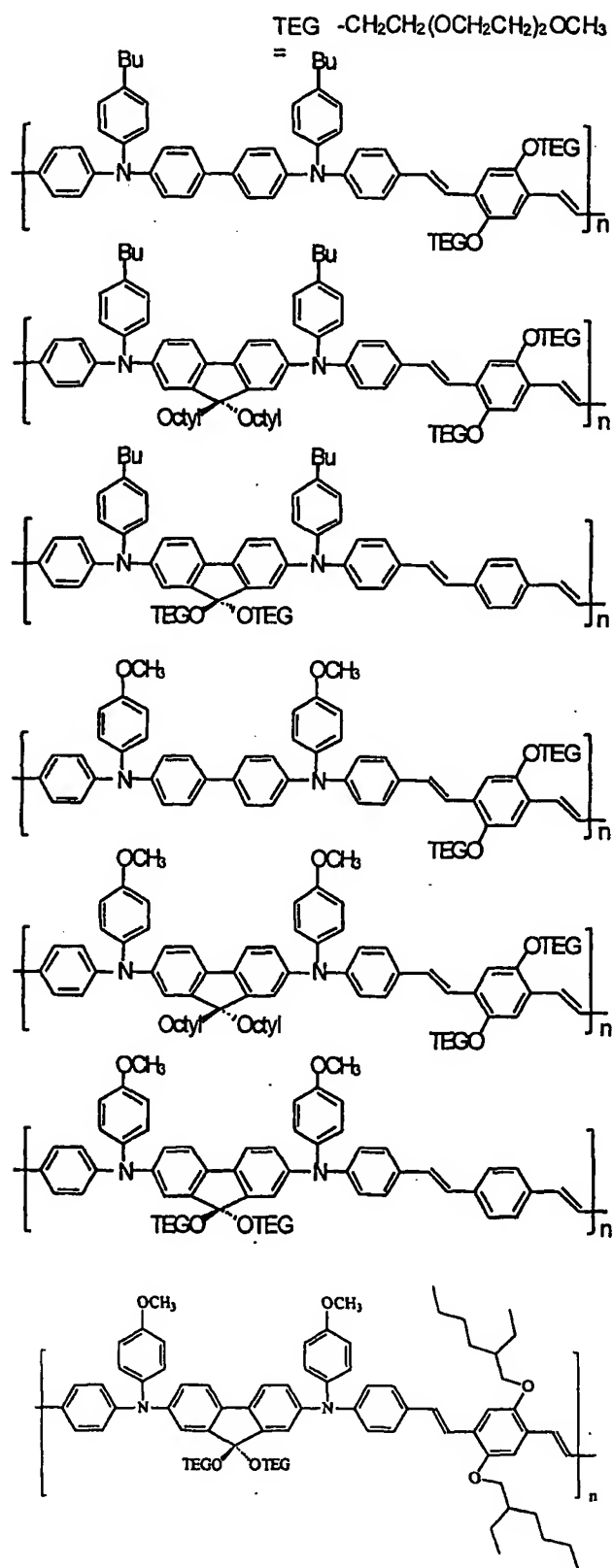


Some illustrative examples of polymers according to the present invention are shown below

5







General Experimental Procedures

¹H-NMR spectra: These were recorded on Bruker DPX-250 (250 MHz) and Bruker DRX-500 (500 MHz) instruments using deuteriochloroform or deuterobenzene as an internal deuterium lock. The chemical shift data for each signal are given in units of δ relative to tetramethylsilane (TMS) where $\delta(\text{TMS}) = 0.00$ ppm. The multiplicity of the signal is indicated as : s - singlet, d - doublet, t - triplet, q - quartet, qu - quintet, br - broad, m - multiplet, dd - doublet of doublets, dt - doublet of triplets *etc.* Coupling constants (*J*) are quoted in Hz.

¹³C-NMR spectra: These were recorded on Bruker DPX-250 (62.5 MHz) and DRX-500 (500 MHz) instruments using an internal deuterium lock and proton decoupling. The chemical shift data for each signal are given in units of δ relative to tetramethylsilane (TMS) where $\delta(\text{TMS}) = 0.00$ ppm. The multiplicity of the signal was determined by APT (Attached Proton Test) experiments.

Infrared spectra: These were recorded on a Perkin-Elmer 1600 series FTIR spectrometer (CCl₄).

Mass spectra: These were recorded by the Mass Spectrometry Services of the University of Swansea or the University of Cambridge. In Swansea, Electron Impact (EI), Electron Spray (ES) and Chemical Ionisation (CI) low resolution spectra were carried out on a VG model 12-253 under ACE conditions. Accurate mass measurements for EI, ES and CI were performed on a +VG ZAB-E instrument. In Cambridge EI, and CI low resolution and accurate mass spectra were performed on a Kratos MS-890. Electrospray spectra were determined with an ES Bruker FTICR. All CI measurements were performed with NH₃ as the carrier gas.

Melting Points: Melting points were determined using a Büchi 510 melting point apparatus, and are uncorrected.

Chromatography: Flash chromatography was carried out on silica gel [Merck 9385 Kieselgel 60 (230-400 ASTM)]. TLC was performed on 0.25 mm thick plates precoated with Merck Kieselgel 60 F254 silica gel.

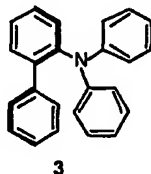
Solvents: Dry THF was distilled from potassium in a recycling still using benzophenone ketyl as indicator. All other solvents were distilled by the support staff at the University of Cambridge Chemical Laboratory.

Glassware was heated prior to use with a gas flame and then cooled with nitrogen.

All reagents except liquids for amination reactions were weighed in the glove box.

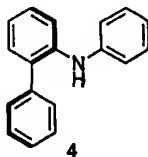
The invention is particularly described in the following working examples. The invention should not be considered to be limited by these working examples.

5 **2-(Diphenylamino)biphenyl (3)**



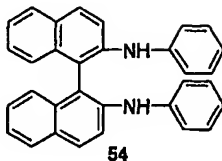
To a solution of diphenylamine (98 mg, 0.58 mmol), Pd(OAc)₂ (1.2 mg, 0.0058
10 mmol) and NaO^tBu (68 mg, 0.7 mmol) in toluene (2 cm³) under nitrogen was
transferred a solution of 2-bromobiphenyl (140 mg, 0.58 mmol) in toluene (1 cm³) and
the reaction mixture was stirred at 50 °C for 10 min. A solution of P(^tBu)₃ (1.2 mg,
0.0058 mmol) in toluene (1 cm³) was injected to the mixture and the reaction heated at
90 °C for 5h. The reaction mixture was directly chromatographed (petroleum ether (40-
15 60) to 1:4 petroleum ether:ether v/v) affording the amine (150 mg, 80%) as a white solid.

2-(Phenylamino)biphenyl (4)



20

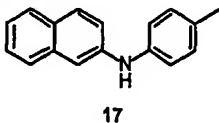
To a solution of 2-aminobiphenyl (144 mg, 0.85 mmol), Pd(OAc)₂ (5.7 mg,
0.0085 mmol) and NaO^tBu (195 mg, 2.03 mmol) in toluene (2 cm³) under nitrogen was
transferred a solution of bromobenzene (266 mg, 1.7 mmol) in toluene (1 cm³) and the
reaction mixture was stirred at 50 °C for 10 min. A solution of P(*t*-Bu)₃ (1.7 mg, 0.0085
25 mmol) in toluene (1 cm³) was injected to the mixture and the reaction heated overnight
at 90 °C. The reaction mixture was directly chromatographed (petroleum ether (40-60)
to 1:4 petroleum ether:ether v/v) affording the amine (32 mg, 16%). as a pink oil.

2,2'-Bis(phenylamino)-1,1'-binaphthyl (54)

5

To a solution of 1,1'-bi-2-naphthylamine (142 mg, 0.5 mmol), Cs₂CO₃ (600 mg, 6 mmol), Pd(dba)₂ (45 mg, 0.05 mmol) and BINAP (50 mg, 0.08 mmol) in toluene (5 cm³) was injected a solution of iodobenzene (1 g, 5 mmol) in toluene (1 cm³) and the reaction mixture was stirred at 85 °C for 18 h. The reaction mixture was directly chromatographed (toluene) affording the product **54** (196 mg, 90%) as an amorphous solid.

10

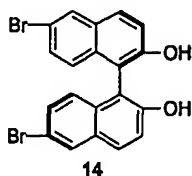
***N, N'*-(2-Naphthy-4-methylphenyl)amine (17)**

15

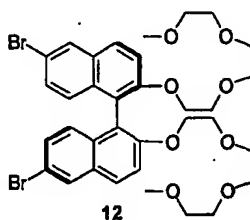
(The use of 2-bromonaphthyl instead of 2-bromonaphthylnonaflate)

2-Bromonaphthyl (6.4 g, 30 mmol), p-toluidine (3.8 g, 36 mmol), Pd(dba)₂ (70 mg, 0.116 mmol), BINAP (140 mg, 0.225 mmol) and NaO^tBu (4.5 g, 40 mmol) were weighed in the glove box. Toluene (30 cm³) was injected and the reaction mixture was stirred overnight at 90 °C. The reaction mixture was filtered with filter paper to remove insoluble part and the solution was directly chromatographed on silica (10 :1 to 5:1 hexane: ether v/v) affording the crude (6.7 g, 96%) as a pale brown solid. This was sublimed at 125 °C (0.2 mmHg) to afford the amine (6.2 g, 87 %) as a white solid.

25

6,6'-Dibromo-2,2'-hydroxy-1,1'-binaphthyl (14)

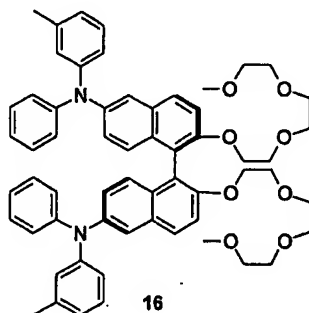
5 To a solution of 2,2'-binaphthol (7.0 g, 24.45 mmol) in dichloromethane (30 cm³) at room temperature was added bromine (8.2 g, 51.33 mmol). Solution was stirred for 5 h. The mixture was poured into saturated sodium thiosulfate water (30 cm³) and stirred until the red colour disappeared. The aqueous layer was extracted with dichloromethane (100 cm³), and the combined organic layers were washed with brine and dried over magnesium sulphate. The solvent was evaporated under reduced pressure to yield brown gel. The crude was then subjected to flash chromatography (6:4 hexane:ethyl acetate v/v) to yield the product 14 (12 g, 93 %) as a white solid.

6,6'-dibromo-2,2'-bis(trisethoxymethoxy)-1,1'-binaphthyl (12)

Potassium *t*-butoxide (1.37 g, 12.2 mmol) was added to stirred solution of the dibromohydroxy binaphthyl (2.46 g, 5.54 mmol) in dried THF (30 cm³). The mixture was stirred at 60 °C for 30 min, and then allowed to cool to room temperature. A solution of tosylated alcohol TsO(CH₂CH₂O)₃CH₃ (3.88 g, 12.2 mmol) in dry THF (30 cm³) was added dropwise into the reaction mixture and stirred at 78 °C for 18 h under a nitrogen atmosphere. The mixture was allowed to room temperature, the solvent removed under pressure and the residue taken up in ether (30 cm³). The ether layer was washed with NaOH solution (10% w/v, 5 x 30 cm³), water (2 x 30 cm³) and dried over

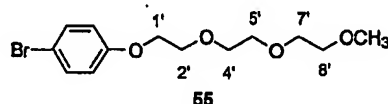
MgSO₄. The solvent was removed *in vacuo* to give a liquid crude. The product was purified by flash chromatography (1:2 hexane:ethyl acetate v/v) to yield the product 12 as brown liquid (3.05 g, 75%).

5 **6,6'-Bis(3-methyldiphenylamino)-2,2'-bis(trisethoxymethoxy)-1,1'-binaphthyl (16)**



Dibromo-TEG-binaphthyl (1.89 g, 2.477 mmol), 3-methyldiphenylamine (1.0 g, 5.44 mmol), Pd(OAc)₂ (33 mg, 0.049 mmol), NaO^tBu (856 mg, 9 mmol) and P(^tBu)₃ (18 mg, 0.098 mmol) in toluene (20 cm³) were stirred at 80 °C under nitrogen for 3 h. After removal of the solvent, followed by dilution with dichloromethane (50 cm³), insoluble parts were removed by filtration with silica gel and washed with plenty of dichloromethane. The solvent was reduced with a rotary evaporator and then poured into
 15 water. The layers were separated and the aqueous layer was extracted with dichloromethane (2x20 cm³). The combined organic layers were dried over MgSO₄. The dichloromethane were evaporated and purified by flash chromatography (1:2 hexane:ethyl acetate v/v) to yield 16 as viscous liquid (2.1 g, 92%).

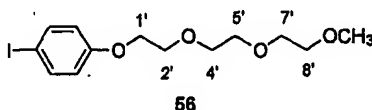
20 ***p*-Trisethoxymethoxy bromobenzene (55)**



Potassium *t*-butoxide (7.24 g, 64.5 mmol) was added to stirred solution of the *p*-
 25 bromophenol (10.1 g, 58.6 mmol) in dried THF (100 cm³). The mixture was stirred under nitrogen at 70 °C for 2 h, and then allowed to cool to room temperature. A

solution of tosylated alcohol $\text{TsO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ (18.7 g, 58.6 mmol) in dry THF (30 cm^3) was added dropwise into the reaction mixture and refluxed overnight under nitrogen. The mixture was allowed to room temperature, the solvent was removed under pressure and the residue was taken up in ether (50 cm^3). The ether layer was washed with NaOH solution (10% w/v, 5 x 30 cm^3), water (2 x 30 cm^3) and dried over MgSO_4 . The solvent was removed *in vacuo* to give a liquid crude. The product was purified by flash chromatography (1:1 petroleum ether(40-60):ether v/v) to yield the product **55** as a colourless liquid (16.2 g, 87%).

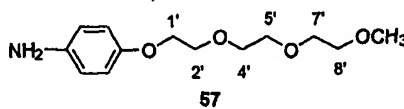
10 *p*-Trisethoxymethoxy iodobenzene (**56**)



Potassium *t*-butoxide (1.60 g, 13.1 mmol) was added to a stirred solution of *p*-iodophenol (2.4 g, 10.9 mmol) in dried THF (40 cm^3). The mixture was stirred under nitrogen at 60 °C for 2 h, and then allowed to cool to room temperature. A solution of tosylated alcohol $\text{TsO}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ (4.6 g, 14.4 mmol) in dry THF (10 cm^3) was added dropwise into the reaction mixture and refluxed for 2 h under nitrogen. The mixture was allowed to room temperature, the solvent was removed under pressure and the residue was taken up in ether (20 cm^3). The ether layer was washed with NaOH solution (10% w/v, 3 x 20 cm^3), water (2 x 10 cm^3) and dried over MgSO_4 . The solvent was removed *in vacuo* to give a liquid crude. The product was purified by flash chromatography (3:2 petroleum ether(40-60):ether v/v) to yield the product **56** (3.2 g, 80%) as a colourless liquid.

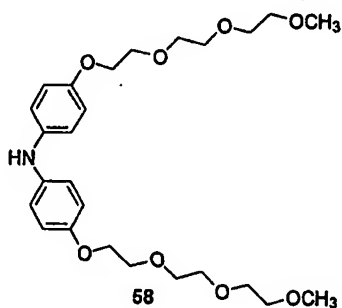
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p-Trisethoxymethoxy aniline (**57**)



Potassium *t*-butoxide (5.5 g, 49 mmol) was added to a stirred solution of 4-aminophenol (4.8 g, 44 mmol) in dried THF (30 cm³). The mixture was stirred under nitrogen at 70 °C for 3 h, and then allowed to cool to room temperature. A solution of tosylated alcohol TsO(CH₂CH₂O)₃CH₃ (14.2 g, 44 mmol) in dry THF (10 cm³) was added dropwise into the reaction mixture and refluxed for 2 h under nitrogen. The mixture was allowed to room temperature, the solvent was removed under pressure and the residue was taken up in ether (20 cm³). The ether layer was washed with NaOH solution (10% w/v, 3 x 20 cm³), water (2 x 10 cm³) and dried over MgSO₄. The solvent was removed *in vacuo* to give a liquid crude. The product was purified by flash chromatography (1:1 to 4:1 hexane:ethyl acetate v/v) to yield the product 57 (10 g, 88%) as a brown liquid.

Bis(*p*-triethoxymethoxyphenyl)amine (58)



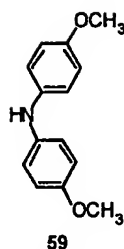
15

To a solution of Pd(dba)₂ (124 mg, 0.2mmol), BINAP (249 mg, 0.4 mmol) and NaO^tBu (1.34g, 14 mmol) in toluene (10 cm³) under nitrogen was transferred a solution of the aniline (3.1 g, 12 mmol) and the bromobenzene (2.9 g, 9.1 mmol) in toluene (20 cm³). The reaction mixture was stirred overnight at 90 °C.

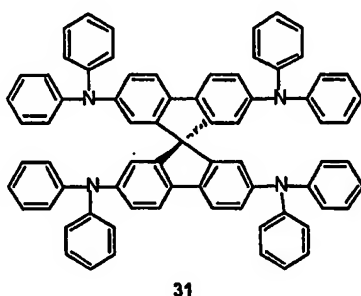
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The reaction mixture was filtered with filter paper to remove insoluble part and the solvent was reduced under pressure. The residue was directly chromatographed on silica (2.5:2:0.5 ethylacetate:dichloromethane:methanol v/v) to yield the product as a brown gel (4.0 g, 87%).

25

4,4'-Dimethoxyphenylamine (59)

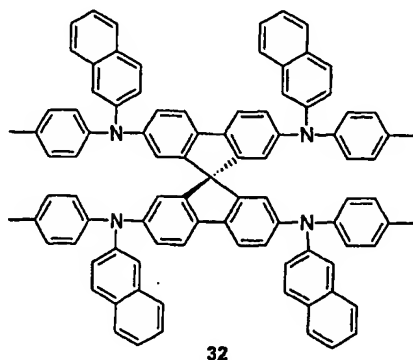
5 To a solution of *p*-anisidine (4.5 g, 36 mmol), Pd(dba)₂ (70 mg, 0.116 mmol), BINAP (140 mg, 0.225 mmol) and NaO^tBu (4.5 g, 40 mmol) in toluene (25 cm³) was injected a solution of 4-bromoanisole (5.6 g, 30 mmol) in toluene (5 cm³) and the reaction mixture was stirred overnight at 90 °C. The reaction mixture was filtered with filter paper to remove insoluble part and the solution was directly chromatographed on silica (10:1 to 2:1 hexane: ethyl acetate v/v) affording the crude (5.2 g, 76%) as a brown solid. This was sublimated at 140 °C (0.2 mmHg) affording the amine (4.3 g, 63 %) as a white solid.

2,2',7,7'-Tetrakis-(diphenylamino)-9,9'-spirobifluorene (31)

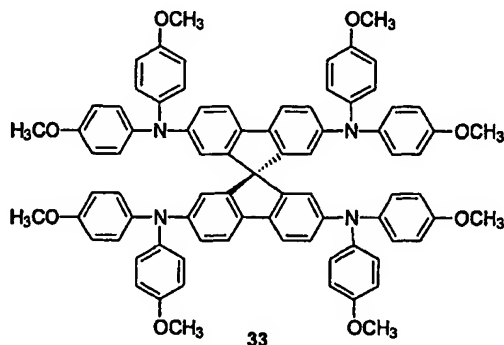
20 To a solution of diphenylamine (841.6 mg, 4.98 mmol), tetrabromospirofluorene (524.8 mg, 0.83 mmol), Pd(OAc)₂ (22 mg, 0.333 mmol) and NaO^tBu (577 mg, 6 mmol) in toluene (9 cm³) was injected a solution of P(*t*-Bu)₃ (13 mg, 0.066 mmol) in toluene (1.0 cm³) and the mixture was stirred under nitrogen at 80 °C for 3 h. After removal of the solvent, followed by dilution with dichloromethane (30 cm³), insoluble parts were

removed by filtration with silica gel and washed with plenty of dichloromethane. The solvent was reduced and then poured into water. The aqueous layer was extracted with dichloromethane (2 x 20 cm³). The combined organic layers were dried over MgSO₄. The solvent was reduced and the resulting residue was purified by flash chromatography (20:1 hexane/ether v/v), followed by recrystallisation (1:10 THF:ethanol v/v) to yield the product 31 as white solid (725 mg, 92 %).

2,2',7,7'-Tetrakis-[*N,N'*-(2-naphthyl-4-methylphenyl)amino]-9,9'-spirobifluorene (32)



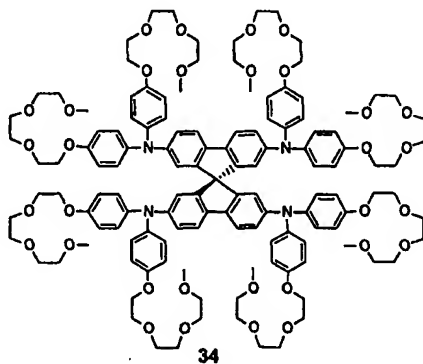
To a solution of *N,N'*-(2-naphthyl-*p*-tolyl)amine (289 mg, 1.24 mmol), tetrabromospirofluorene (196 mg, 0.31 mmol), Pd(OAc)₂ (8.6 mg, 0.012 mmol) and NaO^{*t*}Bu (173 mg, 1.8 mmol) in toluene (5 cm³) was injected a solution of P(*t*-Bu)₃ (9.7 mg, 0.048 mmol) in toluene (1.0 cm³) and the mixture was stirred under nitrogen at 90 °C for 3 h. After removal of the solvent, followed by dilution with dichloromethane (30 cm³), insoluble parts were removed by filtration with silica gel and washed with plenty of dichloromethane. The solvent was reduced and then poured into water. The aqueous layer was extracted with dichloromethane (2 x 10 cm³). The combined organic layers were dried over MgSO₄. The solvent was reduced and the resulting residue was purified by flash chromatography (9:1 cyclohexane/dichloromethane v/v), followed by recrystallisation (1:10 THF:ethanol v/v) to yield the product 32 as pale green solid (250 mg, 64 %).

2,2',7,7'-Tetrakis-di(*p*-methoxyphenylamino)-9,9'-spirobifluorene (33)

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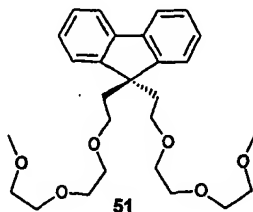
To a solution of di(*p*-methoxyphenyl)amine (912 mg, 4.0 mmol), tetrabromospirofluorene (500 mg, 0.79 mmol), Pd(OAc)₂ (10.8 mg, 0.016 mmol) and NaO^{*t*}Bu (461 mg, 4.8 mmol) in toluene (25 cm³) was injected a solution of P(*t*-Bu)₃ (6.5 mg, 0.032 mmol) in toluene (1.0 cm³) and the mixture was stirred under nitrogen at 90 °C for 2 h. Insoluble parts were removed by filtration with filter paper. The reaction mixture was directly subjected to flash chromatography (petroleum ether (40-60) to 1:2 petroleum ether:ethyl acetate v/v) to yield the crude as dark green solid (890 mg, 92%), which was dissolved in THF (5 cm³) and then precipitated in methanol (200 cm³) affording the product 33 (813 mg, 84 %).

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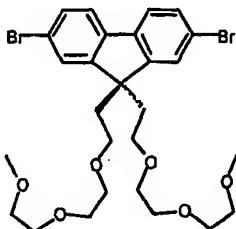
2,2',7,7'-Tetrakis-di(*p*-trisethoxymethoxyphenyl)amino)-9,9'-spirobifluorene (34)

To a solution of tetrabromospirofluorene (171.4 mg, 0.271 mmol), Pd(OAc)₂ (3.7 mg, 0.0054 mmol) and NaO^tBu (77 mg, 1.3 mmol) in toluene (6 cm³) was injected a solution of bis(*p*-trisethoxymethoxyphenyl)amine (535.1 mg, 1.085 mmol) in toluene (10 cm³). The mixture was stirred at 50 °C for approx. 20 min. A solution of P(*t*-Bu)₃ (2.2 mg, 0.108 mmol) in toluene (1 cm³) was injected to the mixture and the reaction mixture was stirred overnight under nitrogen at 90 °C. Insoluble parts were removed by filtration with filter paper. The reaction mixture was directly subjected to flash chromatography (1:1: 0.1 dichloromethane:ethylacetate:methanol v/v) to yield the product 34 (494 mg, 80 %).

9-Bis[2-(2-(2-methoxy-ethoxy)ethoxy)]ethylfluorene (51)



s-BuLi (10.1 cm³, 17.25 mmol, 1.7 M in cyclohexane) was added under nitrogen to a stirred solution of the fluorene (2.867 g, 17.25 mmol) in dried THF (50 cm³) at -80 °C. The mixture was stirred at -78 °C for 40 min. A solution of tosylated alcohol (5.49 g, 17.25 mmol) in dry THF (20 cm³) was added dropwise into the reaction mixture at -78 °C and stirred under nitrogen at room temperature for 4 h. These reactions were repeated. A saturated NH₄Cl solution (20 cm³) was added to the reaction mixture. After removal of THF, the residue was dissolved in ether (100 cm³) and then poured to water. The layers were separated and the aqueous layer was extracted with ether (3x20 cm³). The combined organic layers were dried over MgSO₄. The solvent was reduced and the resulting residue was purified by flash chromatography (1:2 hexane:ethyl acetate v/v) to yield 51 (6.9 g, 87%) as a yellow oil.

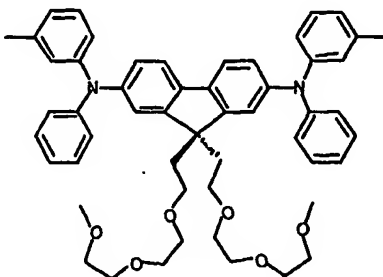
2,7-Dibromo-9-bis[2-(2-(2-methoxy-ethoxy)ethoxy)]ethylfluorene (60)

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To a solution of the fluorene 60 (4.77 g, 0.010 mol) in DMF (20 cm³) was added bromine (3.9 g, 0.024 mol) at 0 °C. The solution was stirred at 0 °C for 10 min. A saturated sodium thiosulphate solution (5 cm³) was dropped to the mixture and stirred until the red colour disappeared. After removal of DMF, the residue was dissolved in
10 dichloromethane (20 cm³) and then poured to water. The aqueous layer was extracted with dichloromethane (3 x 20 cm³) and the combined organic layers were washed with brine and dried over magnesium sulphate. The solvent was reduced and the resulting residue was purified by flash chromatography (1:5 hexane:ether v/v) to afford 5.8 g (92 %)

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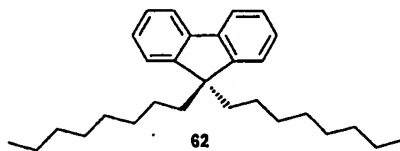
2,7-Bis(3-methyldiphenylamino)-9-bis[2-(2-(2-methoxy-ethoxy)ethoxy)]ethylfluorene (61)

61

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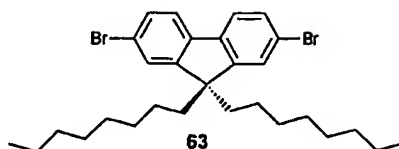
To a solution of Pd(OAc)₂ (18 mg, 0.027 mmol) and NaO^tBu (576 mg, 6 mmol) in toluene (8 cm³) was transferred a solution of 3-methyldiphenylamine (752 mg, 4.1 mmol) and dibromo-TEG-fluorene (859 mg, 1.369 mmol) in toluene (15 cm³). The reaction mixture was stirred at room temperature for approx. 5 min.. A solution of P(*t*-Bu)₃ (10.9 mg, 0.054 mmol) in toluene (1 cm³) was injected to the mixture and the reaction mixture was stirred under nitrogen at 80 °C for 3 h. After removal of the solvent, followed by dilution with dichloromethane (30 cm³), insoluble parts were removed by filtration with silica gel and washed with plenty of dichloromethane. The solvent was reduced and then poured into water. The layers were separated and the aqueous layer was extracted with dichloromethane (2 x 20 cm³). The combined organic layers were dried over MgSO₄. The solvent was reduced and the resulting residue was purified by flash chromatography (1:5 hexane:ether v/v) to yield the product **61** (1.05 g, 93%) as a brown gel.

9-(Diocetyl)fluorene (62)



n-BuLi (15 cm³, 19.85 mmol, 15 % in hexane) was added to stirred solution of the fluorene (1.5 g, 9.0 mmol) in dried THF (40 cm³) at -70 °C. The mixture was stirred under nitrogen at -65 °C for 1 h. A solution of bromooctane (4.2 g, 21.7 mmol) in dry THF (10 cm³) was added dropwise to the reaction mixture at -65 °C and stirred for 30 min. A sat'd NH₄Cl solution (20 cm³) was added to the reaction mixture. After removal of THF, the residue was dissolved in ether (100 cm³). The aqueous layer was extracted with ether (3x20 cm³) and the combined organic layers were dried over MgSO₄. The solvent was reduced and the resulting residue was purified by flash chromatography (petroleum ether) to yield **62** as a colourless oil (3.3 g, 94%).

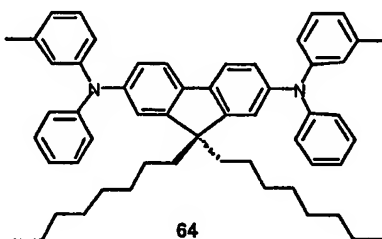
37

2,7-Dibromo-9-(dioctyl)fluorene (63)

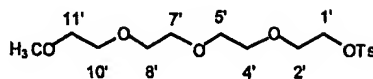
- 5 To a solution of the fluorene (3.54 g, 9.07 mmol) and iodine (228 mg, 0.9 mmol) in dichloromethane (50 cm³) was added bromine (2.9 g, 18 mmol) at room temperature. The solution was stirred overnight under nitrogen. A sat'd sodium thiosulphate solution (20 cm³) was dropped to the mixture and stirred until the red colour disappeared. The aqueous layer was extracted with dichloromethane (3 x 10 cm³) and the combined
10 organic layers were washed with brine and dried over magnesium sulphate. The solvent was reduced and the resulting residue was purified by flash chromatography (petroleum ether) to afford the product 63 (4.6 g, 93 %) as a white solid.

2,7-Bis(3'-methyldiphenylamino)-9-(dioctyl)fluorene (64)

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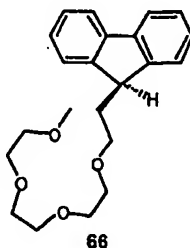
- To a solution of Pd(OAc)₂ (12.5 mg, 0.0185 mmol) and NaO^tBu (427 mg, 4.44 mmol) in toluene (10 cm³) was transferred a solution of 3-methyldiphenylamine (678
20 mg, 3.7 mmol) and the fluorene (1.0 g, 1.85 mmol) in toluene (15 cm³). The reaction mixture was stirred at room temperature for approx. 10 min.. A solution of P(*t*-Bu)₃ (7.5 mg, 0.037 mmol) in toluene (1 cm³) was injected to the mixture and the reaction mixture was stirred under nitrogen at 90 °C for 2 h. Insoluble parts were removed by filtration with filter paper. The solvent was reduced and the resulting residue was purified by
25 flash chromatography (petroleum ether (40-60) to 4:0.7:0.1 petroleum ether:ether:methanol v/v) to yield the product 64 (1.27 g, 91%) as a yellow gel.

3',6',9',12'-Tetraoxaundecanoxyl-1'-*p*-tosylate (65)**65**

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To a stirred solution of tetraethylene glycol monomethyl ether (20 g, 96 mmol) and tosyl chloride (17.75 g, 93 mmol) in dichloromethane (100 cm³) was added triethylamine (14 g, 134 mmol) at 0 °C. The mixture was stirred overnight at room temperature, poured into a stirred solution of HCl in ice water and extracted with dichloromethane. The combined organic extracts were washed with water and dried over magnesium sulphate. The solvent evaporated under reduced pressure to yield a yellow liquid. The crude was then subjected to flash chromatography (1:2 to 2:1 ether:hexane v/v) to yield the tosylated alcohol TsO(CH₂CH₂O)₄CH₃ **65** (27.2 g, 95 %) as a pale yellow liquid.

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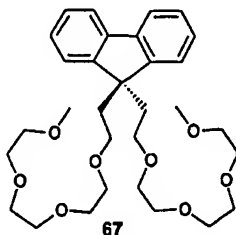
9-[2'-(2'-(2'-(2'-Methoxy-ethoxy)ethoxy)ethoxy)]ethylfluorene (66)**66**

s-BuLi (78 cm³, 101 mmol, 1.3 M in cyclohexane) was added to stirred solution of the fluorene (15 g, 90 mmol) in dried THF (250 cm³) at -70 °C. The mixture was stirred under nitrogen at -70 °C for 2 h. A solution of the tosylated alcohol **65** (29 g, 97 mmol) in dry THF (30 cm³) was dropwised to the reaction mixture at -70 °C and stirred for 4 h. A sat'd NH₄Cl solution (20 cm³) was added to the reaction mixture. After removal of THF, the residue was dissolved in ether (150 cm³). The aqueous layer was extracted with ether (3x50 cm³) and the combined organic layers were dried over

25

MgSO₄. The solvent was reduced and the resulting residue was purified by flash chromatography (hexane to 1:2 hexane:ethyl acetate v/v) to yield the mono substituted product **66** as a pale yellow oil (12.3 g, 35%).

5 **9-Bis[2'-(2'-(2'-(2'-methoxy-ethoxy)ethoxy)ethoxy)ethoxy]ethylfluorene (67)**



(Synthesis from the mono substituted fluorene)

- 10 *s*-BuLi (8.63 cm³, 11.22 mmol, 1.3 M in cyclohexane) was added under nitrogen to a stirred solution of the mono substituted fluorene (4.0 g, 11.22 mmol) in dried THF (40 cm³) at -70 °C. The mixture was stirred at room temperature for 1 h. A solution of the tosylated alcohol **65** (3.35 g, 11.22 mmol) in dry THF (10 cm³) was added dropwise into the reaction mixture at -60 °C and stirred under nitrogen at room temperature for 2
15 h.

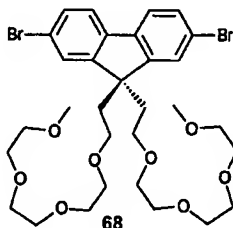
- A saturated NH₄Cl solution (20 cm³) was added to the reaction mixture. After removal of THF, the residue was dissolved in ether (40 cm³) and then poured to water. The layers were separated and the aqueous layer was extracted with ether (3x20 cm³). The combined organic layers were dried over MgSO₄. The solvent was reduced and the
20 resulting residue was purified by flash chromatography (1:4:0 to 1:4:0.1 petroleum ether:(40-60):ether:methanol v/v) to yield **67** (5.4 g, 89 %) as a pale yellow oil

(*In situ* 2 step reactions)

- s*-BuLi (3.85 cm³, 5.0 mmol, 1.3 M in cyclohexane) was added under nitrogen to a
25 stirred solution of the fluorene (0.83 g, 5 mmol) in dried THF (30 cm³) at -70 °C. The mixture was stirred at -70 °C for 1 h. A solution of the tosylated alcohol **65** (1.49 g, 5.0 mmol) in dry THF (10 cm³) was added drop-wise into the reaction mixture at -70 °C and stirred under nitrogen at room temperature for 4 h. These reactions were repeated. A

saturated NH_4Cl solution (20 cm^3) was added to the reaction mixture. After removal of THF, the residue was dissolved in ether (30 cm^3) and then poured to water. The layers were separated and the aqueous layer was extracted with ether ($3 \times 10 \text{ cm}^3$). The combined organic layers were dried over MgSO_4 . The solvent was reduced and the resulting residue was purified by flash chromatography (1:4:0 to 1:4:0.1 petroleum ether (40-60):ether:methanol v/v) to yield **67** (1.5 g, 55 %) as a pale yellow oil.

2,7-Dibromo-9-bis[2'-(2'-(2'-(2'-methoxy-ethoxy)ethoxy)ethoxy)ethoxy]ethylfluorene (68)



(Reaction in DMF without a catalyst)

To a solution of the fluorene (3.68 g, 6.73 mmol) in DMF (30 cm^3) at 0°C was added bromine (0.83 cm^3 , 2.58 g, 16.15 mmol). Solution was stirred at 0°C for 10 min. Saturated sodium thiosulphate solution (10 cm^3) was dropped to the mixture and stirred until the red colour disappeared. After removal of DMF, the residue was dissolved in dichloromethane (30 cm^3) and then poured to water. The aqueous layer was extracted with dichloromethane ($3 \times 20 \text{ cm}^3$), and the combined organic layers were washed with brine and dried over magnesium sulphate. The solvent was reduced and the resulting residue was purified by flash chromatography (1:3 petroleum ether (40-60):ethyl acetate v/v) to yield **68** (1.9 g, 40 %) as a pale yellow oil.

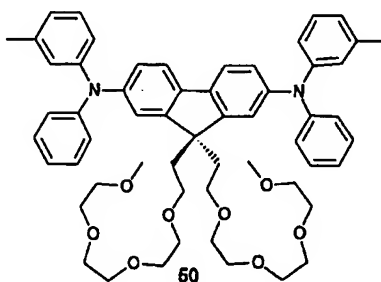
(The use of iodine as a catalyst in dichloromethane)

To a solution of the fluorene (3.68 g, 6.73 mmol) in dichloromethane (40 cm^3) at room temperature was added iodine (173 mg, 0.68 mmol) and bromine (0.83 cm^3 , 2.58 g, 16.15 mmol). Solution was stirred under nitrogen at room temperature for 6 h. Saturated sodium thiosulfate solution (10 cm^3) was dropped to the mixture and stirred until the red colour disappeared. The aqueous layer was extracted with dichloromethane

(3 x 20 cm³), and the combined organic layers were washed with brine and dried over magnesium sulphate. The solvent was reduced and the resulting residue was purified by flash chromatography (1:3 petroleum ether (40-60):ethyl acetate v/v) to yield **68** (4.4 g, 94 %) as a pale yellow oil.

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2,7-Bis(3'-methyldiphenylamino)-9-bis[2'-(2'-(2'-(2'-methoxyethoxy)ethoxy)ethoxy)]ethylfluorene (50)

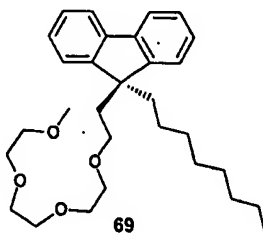


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To a solution of Pd(OAc)₂ (13.5 mg, 0.02 mmol) and NaO^tBu (780 mg, 8 mmol) in toluene (10 cm³) was transferred a solution of 3-methyldiphenylamine (1.1 g, 6 mmol) and the fluorene (1.4 g, 2 mmol) in toluene (15 cm³). The reaction mixture was stirred at room temperature for approx. 10 min.. A solution of P(*t*-Bu)₃ (8 mg, 0.04 mmol) in toluene (1 cm³) was injected to the mixture and the reaction mixture was stirred under nitrogen at 90 °C for 4 h. Insoluble parts were removed by filtration with filter paper. The solvent was reduced and the resulting residue was purified by flash chromatography (1:5 petroleum ether (40-60):ether to ether v/v) to yield the product **50** (1.4 g, 96 %) as a brown gel.

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9-[2'-(2'-(2'-(2'-methoxy-ethoxy)ethoxy)ethoxy)]ethyl-octylfluorene (69)

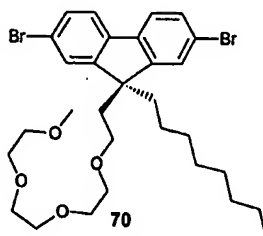


69

t-BuLi (15.5 cm³, 9.2 mmol, 1.7 M in pentane) was added under nitrogen to a stirred solution of the mono substituted fluorene (5.0 g, 14.1 mmol) in dried THF (80 cm³) at -70 °C. The mixture was stirred at room temperature for 2 h. Octylbromide (3.3 g, 17.1 mmol) in dry THF (10 cm³) was slowly transferred to the reaction mixture at -68 °C and stirred under nitrogen at room temperature for 40 min.

A saturated NH₄Cl solution (20 cm³) was added to the reaction mixture. After removal of THF, the residue was dissolved in ether (40 cm³) and then poured to water. The layers were separated and the aqueous layer was extracted with ether (3 x 20 cm³). The combined organic layers were dried over MgSO₄. The solvent was reduced and the resulting residue was purified by flash chromatography (1:4 hexane:ether v/v) to yield 69 (5.6 g, 89 %) as a pale yellow oil.

2,7-Dibromo-9-[2'-(2'-(2'-(2'-methoxy-ethoxy)ethoxy)ethoxy)ethoxy]ethyloctylfluorene
(70)



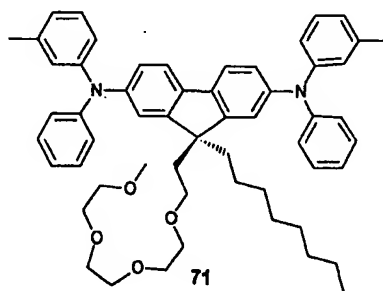
(Reaction in DMF without a catalyst)

To a solution of the fluorene (3.19 g, 6.81 mmol) in DMF (30 cm³) at 0 °C was added bromine (0.85 cm³, 2.62 g, 16.35 mmol). Solution was stirred at 0 °C for 10 min. Saturated sodium thiosulfate solution (10 cm³) was dropped to the mixture and stirred until the red colour disappeared. After removal of DMF, the residue was dissolved in dichloromethane (30 cm³) and then poured to water. The aqueous layer was extracted with dichloromethane (3 x 20 cm³), and the combined organic layers were washed with brine and dried over magnesium sulphate. The solvent was reduced and the resulting residue was purified by flash chromatography (2:3 petroleum ether (40-60):ether v/v) to yield 70 (2.5 g, 60 %) as a pale yellow oil.

(The use of iodine as a catalyst in dichloromethane)

To a solution of the fluorene (3.19 g, 6.81 mmol) in dichloromethane (40 cm³) at room temperature was added iodine (17 mg, 0.67 mmol) and bromine (0.85 cm³, 2.62 g, 16.35 mmol). Solution was stirred under nitrogen at room temperature overnight. Saturated sodium thiosulphate solution (10 cm³) was dropped to the mixture and stirred until the red colour disappeared. The aqueous layer was extracted with dichloromethane (3 x 20 cm³), and the combined organic layers were washed with brine and dried over magnesium sulphate. The solvent was reduced and the resulting residue was purified by flash chromatography (2:3 petroleum ether (40-60):ether v/v) to yield **70** (2.78 g, 64 %) as a pale yellow oil.

2,7-Bis(3'-methyldiphenylamino)-9-bis[2'-(2'-(2'-methoxy-ethoxy)ethoxy)ethoxy]ethylfluorene (71)



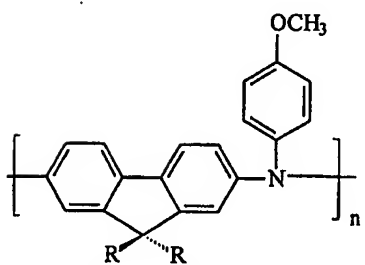
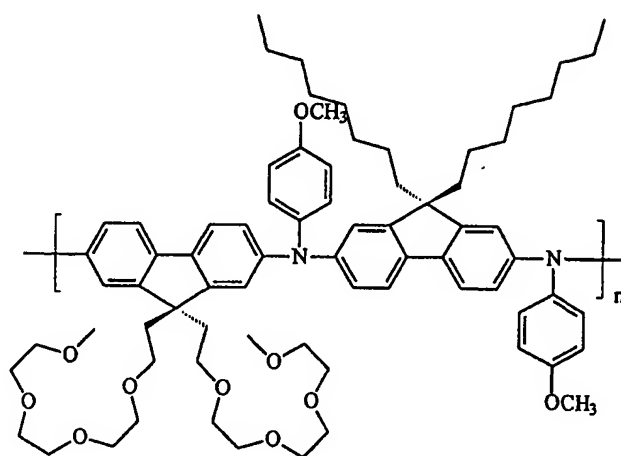
To a solution of Pd(OAc)₂ (19.5 mg, 0.029 mmol) and NaO^tBu (501 mg, 5.2 mmol) in toluene (10 cm³) was transferred a solution of 3-methyldiphenylamine (793 mg, 4.35 mmol) and the fluorene (940 mg, 1.45 mmol) in toluene (10 cm³). The reaction mixture was stirred at room temperature for approx. 10 min.. A solution of P(*t*-Bu)₃ (11.7 mg, 0.058 mmol) in toluene (1 cm³) was injected to the mixture and the reaction mixture was stirred under nitrogen at 90 °C for 4 h. Insoluble parts were removed by filtration with filter paper. The solvent was reduced and the resulting residue was purified by flash chromatography (1:1 to 1:5 petroleum ether (40-60):ether v/v) to yield the product **71** (920 mg, 95 %) as a brown gel.

The molecules of the present invention may be oligomerised or polymerised by methods known in the art. The molecules, or their oligomers or polymers, may be incorporated into solid charge-conducting tracks or films, which may contain other components especially ions such as lithium ions, in known manner. The invention is
5 believed to have particular applications to electro-optic and/or electrochemical devices, such as photovoltaic cells.

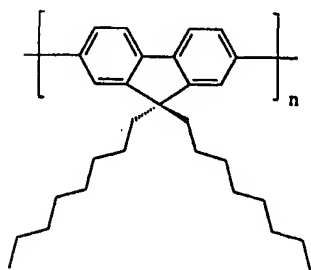
Conductivity Experiments

Polymer	wt% of dopant (SbCl_6^-)		
	0	2	10
[1]	$1.7 \times 10^{-9} \text{ S/cm}$	$3.7 \times 10^{-9} \text{ S/cm}$	$4.4 \times 10^{-8} \text{ S/cm}$
[2]	$1.2 \times 10^{-8} \text{ S/cm}$	$1.4 \times 10^{-7} \text{ S/cm}$	$0.8 \times 10^{-7} \text{ S/cm}$
[3]	$2.3 \times 10^{-7} \text{ S/cm}$	$3.2 \times 10^{-7} \text{ S/cm}$	-
[C1]	$1.3 \times 10^{-10} \text{ S/cm}$	-	-
[C2]	$0.7 \times 10^{-10} \text{ S/cm}$	-	-

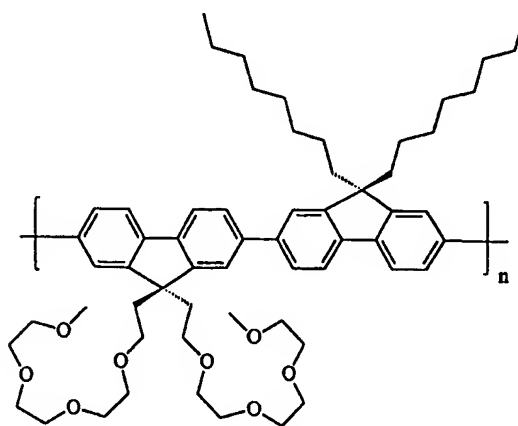
Table 2

[1] $\text{R} = -(\text{CH}_2)_7\text{CH}_3$ [2] $\text{R} = -\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$ 

[3]



[C1]



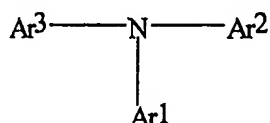
[C2]

Table 2 shows that the conductivity of a tri-arylamine based polymer not according to the invention, polymer [1], is low but improves with increased doping. Polymer [2], according to the invention, incorporates a fluorene substituent derivatised by ion-chelating groups, R. Without doping, it can be seen that the conductivity of this polymer is an order of magnitude greater than undoped polymer [1]. Similar increases are achieved for 2 and 10 wt% doping. A further increase in conductivity is shown for polymer [3] according to the invention, which has two fluorene substituents, one derivatised with ion-chelating groups and a second substituted with two octyl groups. This polymer also shows increased conductivity when compared to polymer [1] with 2 and 10 wt% doping.

By way of comparison, two structurally similar non amine polymers are included in table 2. The conductivities of these are an approximately an order of magnitude lower than that of polymer [1].

CLAIMS:

1. A material for charge transporting, the material comprising tertiary amine molecules or oligomers or polymers thereof, wherein said molecules comprise at least one moiety represented by the general formula (1):



(1)

wherein Ar^1 , Ar^2 and Ar^3 are independently substituted or unsubstituted aromatic or hetero-aromatic rings or fused or otherwise conjugated derivatives thereof; wherein one or more of Ar^1 , Ar^2 and Ar^3 is derivatised with one or more ion-chelating groups selected from $[-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OCH}_3]$, $[-\text{O}(\text{CH}_2\text{CH}_2)_n\text{OCH}_3]$, $[-(\text{CH}_2\text{CH}(\text{R})\text{O})_n\text{CH}_2\text{CH}_2\text{OCH}_3]$ and $[-\text{O}(\text{CH}(\text{R})\text{CH}_2)_n\text{OCH}_3]$; wherein n is an integer from 0 to 10, preferably 2 to 10, more preferably 2 to 4; wherein R is straight or branched alkyl chain of 1 to 10 carbon atoms, preferably of 1 or 2 carbon atoms; and wherein the ion chelating groups comprise side chains in oligomeric or polymeric structures.

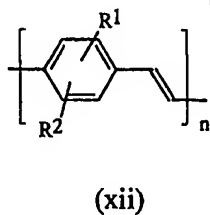
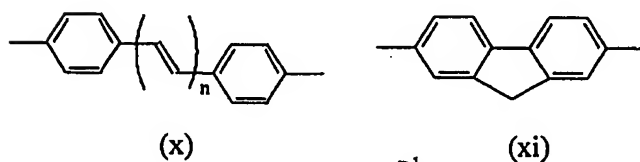
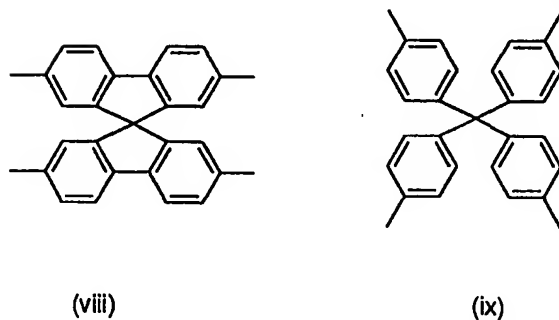
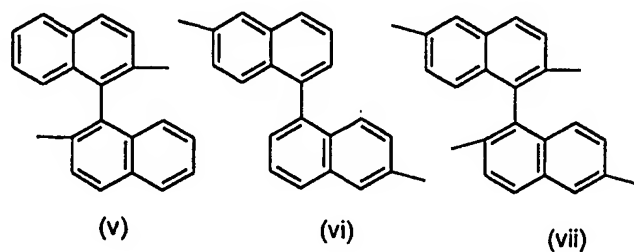
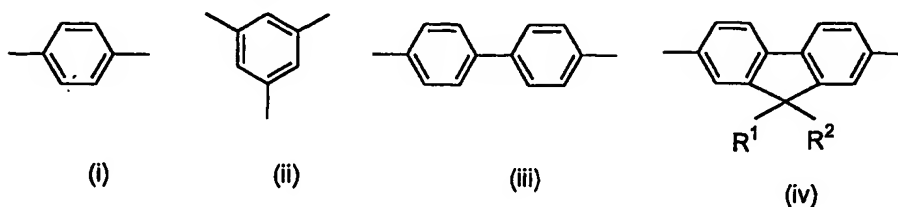
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2. A material according to claim 1, wherein the material exhibits extended π or mixed π -lone pair conjugation.
3. A material according to claim 1 or claim 2, wherein at least one of Ar^1 , Ar^2 or Ar^3 is substituted by alkyl, alkoxy, ether, halo alkyl, amino alkyl, aryl or heteroaryl, where any alkyl group is straight or branched chain of 1-10 carbon atoms.
4. A material according to any preceding claim, wherein at least one of Ar^1 , Ar^2 or Ar^3 is substituted in the ortho- or para- position by an alkoxy group.
5. A material according to claim 4, wherein at least one of Ar^1 , Ar^2 or Ar^3 is substituted in the para- position by an alkoxy group.

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6. A material according to claim 4 or claim 5, wherein the alkoxy group comprises a C1 – C4 alkoxy group.

7. A material according to any preceding claim, wherein at least one of Ar¹, Ar² or Ar³ is selected from structures (i) to (xii)



wherein R¹ and R² are independently selected from, hydrogen, halogen, alkyl, alkoxy, ether, amino alkyl, aryl or heteroaryl, in which any alkyl group is straight or branched

chain of 1 to 10 carbon atoms; wherein n is an integer; and wherein any of (i) to (xii) may be substituted or unsubstituted.

8. A material according to any preceding claim, wherein a further ion-chelating
5 group is used as a linking group in the para-position between moieties of general formula 1.
9. A charge-conducting film or track comprising a material according to any preceding claim.
- 10
10. An electro-optic device comprising a material according to any of claims 1 to 8.
11. A photovoltaic cell comprising a material according to any of claims 1 to 8.
- 15 12. An electrochemical device comprising a material according to any of claims 1 to 8.

INTERNATIONAL SEARCH REPORT

PCT/GB 01/05672

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C09K11/06 H01B1/00 H01L51/30		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 C09K H01B H01L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 54385 A (DOW CHEMICAL CO) 28 October 1999 (1999-10-28) page 1 -page 5; claims 1,7,8	1-12
X	US 5 929 194 A (INBASEKARAN MICHAEL ET AL) 27 July 1999 (1999-07-27) claims 1,2; examples 13-15	1-12
X	EP 0 721 935 A (IDEMITSU KOSAN CO) 17 July 1996 (1996-07-17) page 20; claims 1-9 page 21 page 23 page 26-27 page 33-36	1-12
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 20 February 2002		Date of mailing of the international search report 28/02/2002
Name and mailing address of the ISA European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016		Authorized officer Wengeler, H

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P,X	US 2001/026878 A1 (INBASEKARAN MICHAEL ET AL) 4 October 2001 (2001-10-04) page 3; claims 1,7,8 page 7, line 53-56 -----	1-12

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